In-Situ XAFS Analysis of Redox Reactions for Cu/SiO_2 Catalyst

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1. Introduction

Copper catalysts are widely used to convert CO_2, which arises the global warming, to ethanol by hydrogenation reaction [1]. In addition, it is reported that the small particle of the copper species can realize high catalytic performance for the reductive electrolysis of CO_2 [2]. Therefore, the chemical analysis of the Cu catalyst with small active species is important to improve the catalytic performance and to design a new functional Cu catalyst. It has been revealed that the redox temperatures of the supported Ni species are significantly changed in response to the particle size [3]. The purpose of this study is to clarify the redox property for the SiO_2-supported Cu catalyst with the small particle size prepared by the impregnation method with citric acid (ImpCA) and to compare with the corresponding Cu catalyst prepared by the conventional impregnation method (Imp).

2. Experimental

The SiO_2-supported Cu catalyst was prepared by the Imp method using an aqueous solution of copper nitrate. The stoichiometric amount of citric acid was added into the solution to prepare the small Cu particle by the ImpCA method. The Cu loading was set to be 10 wt% for both preparation methods. The XAFS measurements were carried out at BL-3 of SR Center (Ritsumeikan University) and BL-9C of Photon Factory (KEK). The *in-situ* XAFS experiments were performed at the Cu K edge during the temperature-programmed reduction (TPR) and oxidation (TPO) processes under the dilute H_2 and O_2 atmosphere up to 400 °C and 600 °C, respectively.

3. Results and discussion

The particle size was estimated by the TEM measurements. The average diameter of the Cu

particle prepared by Imp and ImpCA methods were at 18 nm and 11 nm, respectively. The particle size by ImpCA was confirmed to be smaller than that prepared by Imp.

The results of the composition analysis during the TPR process are shown in Figure 1. It is indicated that the reduction from CuO to metallic Cu proceeds at 320 °C and 270 °C for Imp and ImpCA, respectively. The refinement of the CuO particle promotes the lower shift of the reduction temperature by *ca*. 50 °C.

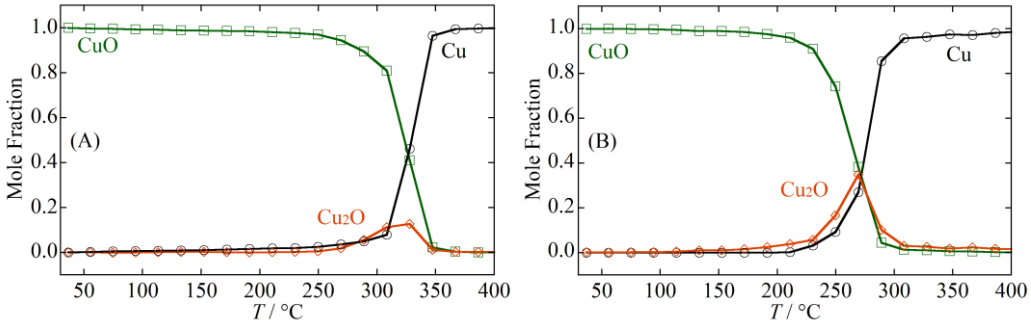
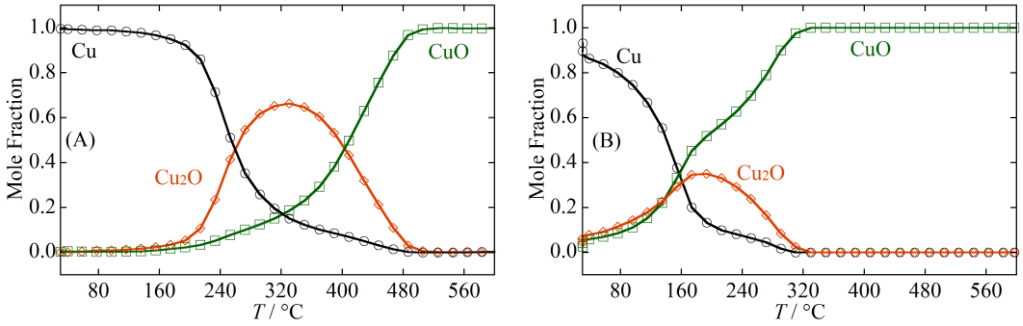


Figure 1 The composition change for the Cu catalyst prepared by the Imp (A) and ImpCA (B) method during the TPR process.

The composition change during the TPO process given in Figure 2 indicates that the oxidation temperature of the small Cu species is lower by *ca*. 160 °C. The present *in-situ* XAFS study revealed that both the redox temperatures are shifted to lower by the refinement of the particle size of the Cu species. The lower shifts of temperature can arise from an easy oxygen migration and a large surface area for the smaller Cu particle.

Figure 2 The composition change for the Cu catalyst prepared by the Imp (A) and ImpCA (B) method



during the TPO process.

References

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